Exact repulsive pressure with "hydration regulation" (solid line)
and linearized theory with fixed polarization (upper dashed line)
and fixed polarization potential (lower dashed line) boundary
condition for F = 10 and 0.1.

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HYDRATION FORCE AND HYDRATION REGULATION

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The phenomenological and the microscopic model of hydration force
between two interfaces immersed in water were used to elucidate
the connection between different boundary conditions used in the
hydration force theory. We argue that these boundary conditions
are merely different limiting forms of the general self-consistent
boundary condition.

Introduction

Recent measurements of forces between zwitterionic and charged
phospholipid multilayers /10, 17, 11, 5/ and between mica plates
/18, 9/ immersed in aqueous solutions clearly show the existence
of additional repulsive force besides the usual Gouy-Chapman re-
pulsion (if present). This additional short range repulsion is
quite   different in nature from the double layer forces /21/ as
it is insensitive to the concentration of the electrolyte and is
usually strong enough to prevent the colloidal system from reach-
ing its primary minimum predicted by the Deryaguin-Landau-Verwey-
-Overbeek (DLVO) theory /23/. Contrary to the DLVO forces this
additional force, or hydration force (generally solvation force)
as it is called, is intrinsically dependent on the presence of the
medium, specifically on the intersolvent coupling as no strong
monotonous solvations force is observed in systems in which large
intersolvent interactions are absent /2/.

Theoretical study of the solvation phenomena is often performed
through the framework of mean-field solvation theories, because
these are relatively simple and versatile. S. Marčelja and his
coworkers were the first to formulate a mean-field Landau-type
approach to the solvation force /14, 12, 13/. They used the

Landau phenomenological expansion of the free energy to predict the polarization field between two parallel plates assuming as a boundary condition that the polarization ($\vec{P}$) is fixed on the plates. The repulsive pressure originating from the polarization profile has an exponential form and agrees nicely with experimental observations.

This was a suggestive start and provided an entry point into the problem though the original Marčelja theory had many drawbacks. Among others NINHAM /15/ numbers also the fact that the boundary condition was not well defined. Subsequent approaches /3, 22/ used different variants of the original boundary condition but were not able to link their choices with some clearly understandable (and perhaps even measurable) properties of the system. It is the object of this note to show how the boundary condition can be obtained in a self-consistent way with no ad hoc assumptions and to construct a microscopic model that would elucidate the meaning of the parameters involved.

Landau expansion

Assuming that the free energy (F) varies slowly with distance we can expand it in terms of symmetry permitted scalar invariants of the vector order parameter $\vec{P}$ /1/:

$$F = \int (- \vec{P}\vec{E}_o + \frac{\alpha}{2} P^2 + \frac{\beta}{2} (\text{div } \vec{P})^2) d^3 \vec{r} \tag{1}$$

where α and β are phenomenological constants. The first term on the r.h.s. of (1) presents the influence of the external field ($\vec{E}_o$), if present, on the free energy. We did not include the higher-order invariants into free energy expansion since in bulk water we demand that $\vec{P} = 0$. Equation (1) presents only the volume part of the free energy while the surface part is given by the Landau expansion in terms of surface scalar invariants /6/:

$$F = \oint (- P_z F_o + \frac{c}{2} P_z^2) \, dS \tag{2}$$

where we have assumed that the normal to the surface points in the z-direction.

Putting (1) and (2) together and performing the first variation we obtained two Euler-Lagrange equations. The first one:

$$\beta \nabla^2 \vec{P} = \alpha \vec{P} - \vec{E}_o \tag{3}$$

simply describes the spatial profile of the order parameter while the second one:

$$\pm c\, P_z - \beta \frac{dP_z}{dz} = F_o \tag{4}$$

self-consistently determines the boundary condition in terms of surface values of order parameter, its derivative and the surface field F_o. The two signs in the first term of the l.h.s. of (4) correspond to two surfaces situated at $z = -a$ and $z = a$. If $\vec{E}_o = 0$ the solution of the system (3, 4) turns out to be:

$$P_z = -F_o \frac{sh(x/\xi)}{(c\; sh(a/\xi) + (\beta/\xi)\; ch(a/\xi))} \tag{5}$$

where we have defined $\xi^2 = \beta/\alpha$. Taking into account (5) we get the free energy (1, 2) in the form:

$$F = -\frac{F_o^2}{c} \frac{\chi\; th(a/\xi)}{1 + \chi\; th(a/\xi)} \tag{6}$$

where $\chi = c\xi/\beta$ and is essentially the ratio between bulk and surface susceptibilities. Two different interesting limiting forms of (6) emerge. If we let $\chi \to 0$ we get from (6) to the lowest order in χ:

$$F = -\frac{F_o^2}{c} \chi\; th(a/\xi) \tag{7}$$

In the opposite limit of $\chi \to \infty$, (6) in the lowest order of χ^{-1} tends towards:

$$F = -\frac{F_o^2}{c} + \frac{F_o^2}{c} \chi^{-1}\; cth(a/\xi) \tag{8}$$

In (7) and (8) we can recognise the two forms of the free energy already available in the literature /3, 14/. The first form corresponds to the free energy obtained in the case of fixed order parameter derivative boundary condition /3/, while the second one is the original Marčelja fixed order parameter boundary condition /14/. The two boundary conditions are thus shown to be only limiting forms of a general self-consistent boundary condition, the limit being dependent on the value of phenomenological parameter χ.

FIG. 1 shows that while (7) and (8) show pronounced discrepancy with purely exponential behaviour the log plot of (6) for $\chi = 1$ is linear in the whole range of a, therefore, conforming closely to the experimental findings on the hydration force.

Microscopic model

Subsequent to the phenomenological theory GRUEN and MARČELJA /8, 7/ came to the conclusion that the microscopic model of nonideal ice can be of some relevance for elucidating the meaning of the phenomenological constants. Their conclusions can be briefly stated in the form that as ions screen the electrostatic field in electrolyte solution so Bjerrum orientational defects screen the polarization in nonideal ice.

While a definite microscopic meaning has thus been attached to constants α and β in (1) the boundary condition has remained in the same ad hoc form. We have ventured to alter this situation by trying to derive that part of the free energy of nonideal ice that is connected with the structure of the surface layer of ice facing its boundaries. We shall not go through all the details of our argument /19/, but shall merely state the result that is an analogon to the phenomenological equation (4):

$$\pm P_z = e_B N \, th(\frac{e_B \, \phi_c}{kT} - F) \tag{9}$$

In (9) P_z is the surface value of the configurational part of polarization, e_B is the charge of the Bjerrm defect, N is the surface density of water molecules in ice, ϕ_c is the polarization associated potential that is proportional to dP_z/dz and F is defined as follows: if the energy difference in the orientation of surface water molecule towards and against the surface is $\Delta\varepsilon$, than F is:

$$F = \frac{1}{2} \frac{\Delta\varepsilon}{kT} \tag{10}$$

Linearising (9) we clearly see that it reduces to a form analogous to (4). Combining (9) and the ice-analogon of (3) /7/ we can construct the spatial profile of polarization and through it the repulsive ("hydration") pressure operating between the two surfaces.

As was the case with the phenomenological model the nature of the

repulsive pressure strongly depends on a paramter of the boundary
condition (9). In this case this is F. If F → ∞ the repulsive
pressure is well described by the linear theory with fixed polar-
ization as the boundary condition. On the contrary, if F is non-
zero and F << 1 the exact repulsive pressure is mimicked by the
linear theory with fixed polarization as the boundary condition.
FIG. 2 presents the repulsive pressure for different values of F
and results of the linearized theory for the two limiting cases
of the boundary condition.

Finally we should make a comment on the derivation of the self-
consistent boundary condition (9) in the case of nonideally bounded
ice. The derivation of (9) can be accomplished by two different
ways. Either we start from the surface part of the free energy
or we can as well start from the process of chemical adsorption
of Bjerrum defects on the surface of ice as each adsorbed Bjerrum
defect changes the orientation of one surface water molecule from
the "towards" to the "away" orientation regarding the surface
normal. As this process of chemical adsorption of Bjerum defect
bears some resemblance to the adsorption of ions in the case of
"charge regulation" /16, 4/ we propose the term "hydration regu-
lation" for the selfconsistent determination of the boundary
polarization (9).

Conclusions

In the present note we have elucidated the connection between
different types of boundary conditions used in the hydration
force theory. We argue that these boundary conditions are mearly
different *limiting forms* of the general "hydration regulated"
boundary condition. Through the microscopic model of nonideally
bounded ice we were able to show that the limiting process is
dependent on the energy difference between the two orientations
of the water molecule at the surface. The self-consistent boundary
condition conforms more closely with experimental data than any of
the two limiting forms. All the relevant details of the calcula-
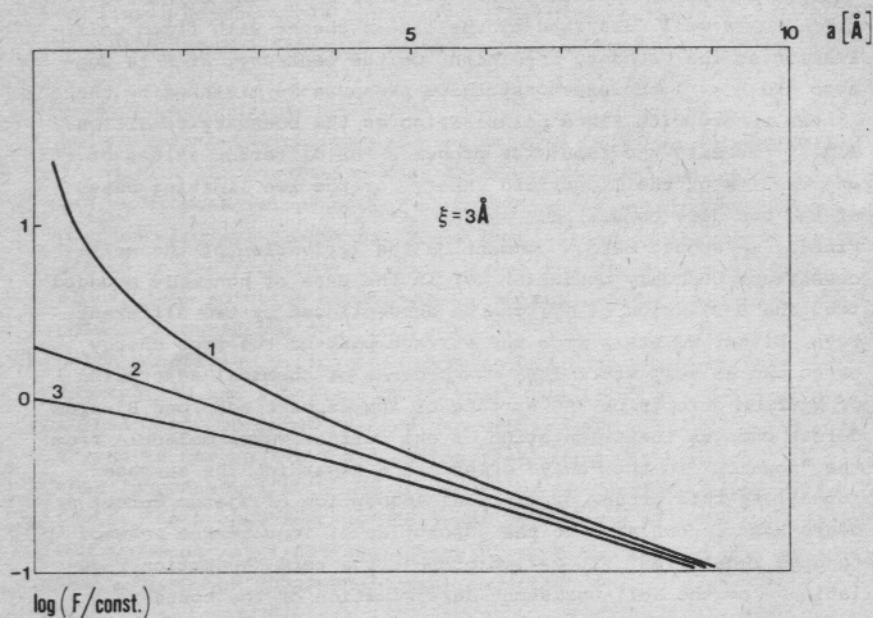tions that were omitted in this report will be published else-
where /20/.

FIG. 1

The interaction free energy, F as a function of interfacial half-distance, a. The selfconsistent boundary condition (curve 2) leads to the exponential behaviour in the whole range of inter-facial distances. The fixed order-paramter boundary condition (curve 1) and fixed order-parameter derivative boundary condition (curve 3) lead to discrepancies at small interfacial separation as compared with purely exponential behaviour as observed in experiments.
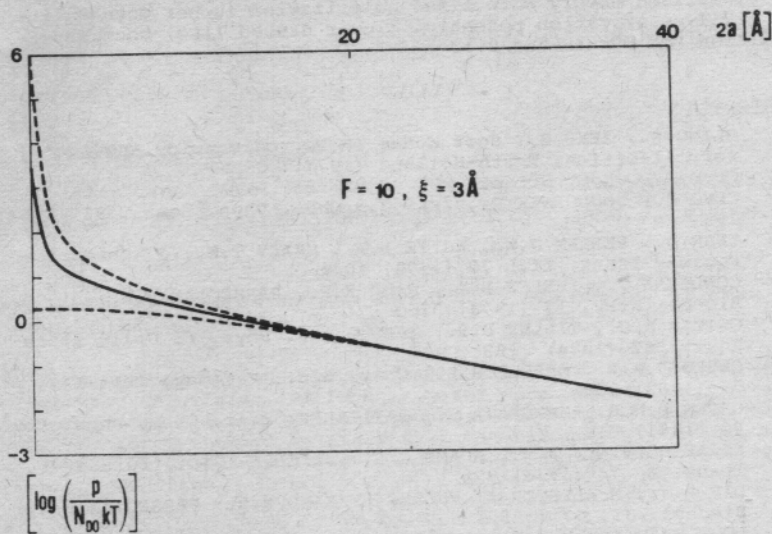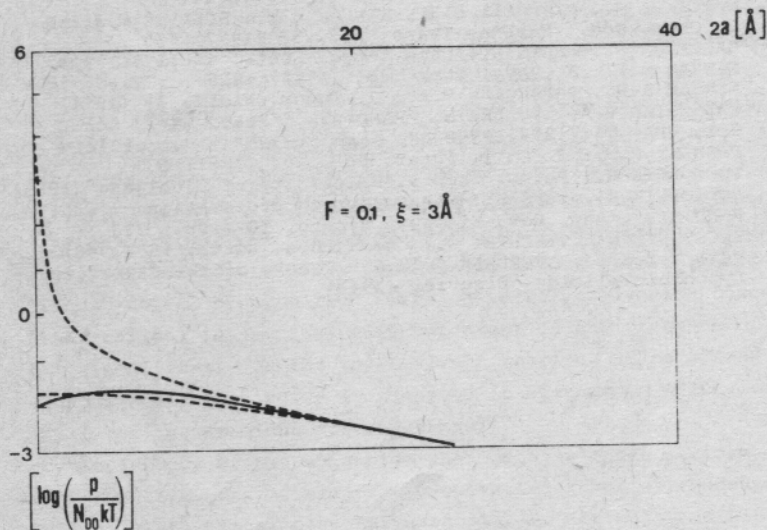
FIG. 2 a

FIG. 2 b